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ICP-MS and HPLC-ICP-MS for large scale monitoring oftotal arsenic and inorganic arsenic in Norwegian seafood

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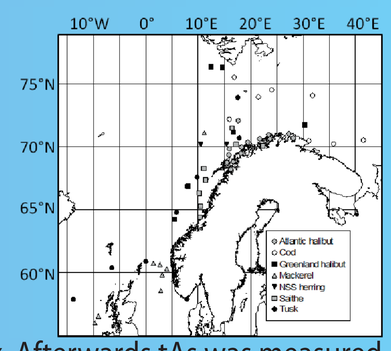
Introduction

Fish and seafood products contain high amounts of arsenic compared to terrestrial food items. The toxicity of As is highly depended on the speciation. Organic bound As (which is the major species in seafood) is much less toxic compared to inorganic As (iAs). iAs such as arsenite and arsenate is highly toxic for mammalians and mayesometimes be present in food such as rice or shellfish. Thus As and iAs should be monitored in food for food safety reasons and for Norwegian seafood products NIFES has the official monitoring duty. The European Food Safety Authority (EFSA) recently issued an opinion on As in food underlining the need for more data on As speciation in various food items. In addition, the need for robust routine monitoring of iAs in food was called upon. Currently only 2% of all 100.000 As food data provided to EFSA from the member states have information on iAs included. The variable amount of iAs in seafood products combined with the limited data made EFSA to propose fixed levels for iAs in seafood (0.03 mg/kg for filet and 0,1 mg/kg for other seafood products) in their exposure calculations. We evaluate here the iAs in nearly 1000 samples from Norway and compare actual levels with EFSA guidelines.

Sampling & Instrumentation

Sampling:
Sampling of cod was done using bottom trawls (IMR), Atlantic mackerel and herring was sampled using pelagic trawl (IMR), Greenland halibut was sampled using longline (IMR) while tusk, saithe and Atlantic halibut were sampled by trawls or nets (IMR). Sample positions are indicated in the map to the right.

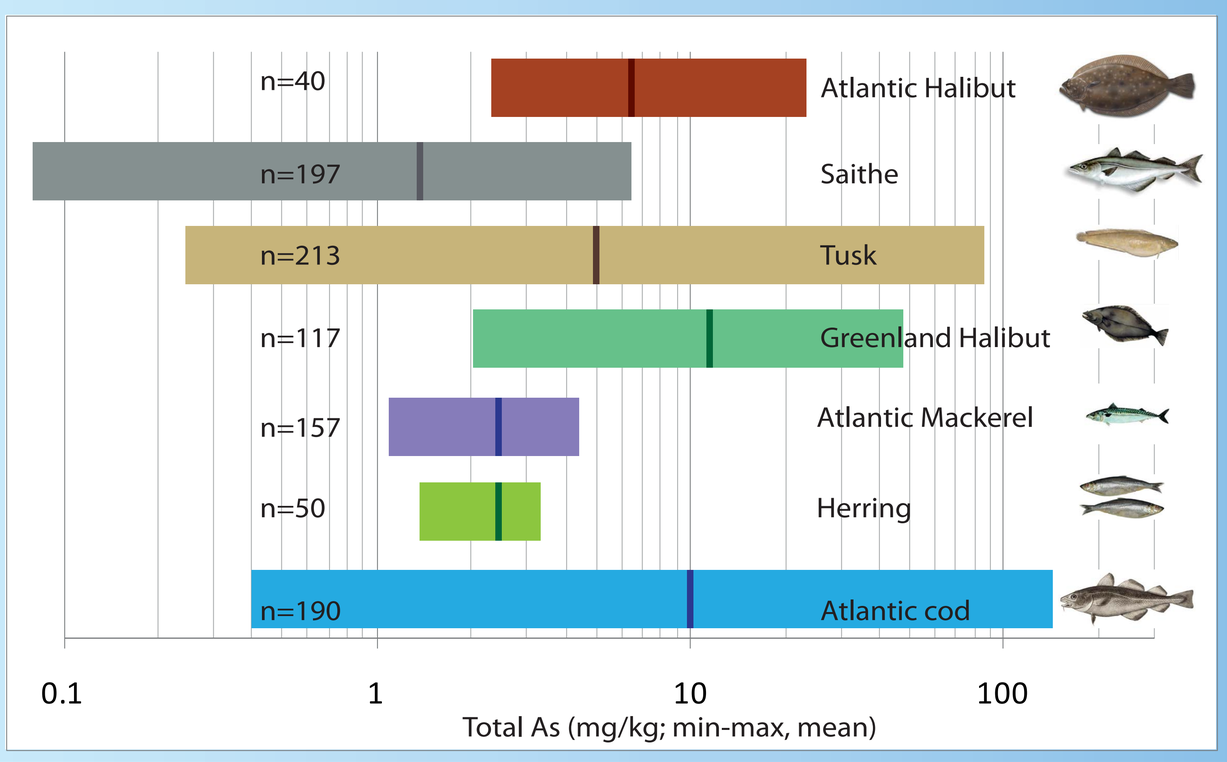


Total Arsenic:
Samples were digested in a microwave oven using a HNO_3/H_2O_2 mix. Afterwards tAs was measured with Q-ICP-MS (Agilent 7500x) using no gas mode with ^{89}Y as internal standard and external calibration. Quality monitoring was done by SRM TORT-2 and NIST SRM 2977.

Inorganic Arsenic:
For iAs samples were leached in a microwave oven with a 0,07 M HCl / 3% H_2O_2 mix. Subsequently samples were analysed by ion exchange HPLC-ICP-MS with 30 mmol L^{-1} $(NH_4)CO_3$ / MeOH as mobile phase in isocratic elution at 1 ml min^{-1} flow rate and using an Agilent 7500c as ICP-MS detector. Quantification was done by external calibration and TORT-2 served as QM standard.

Total arsenic (tAs)

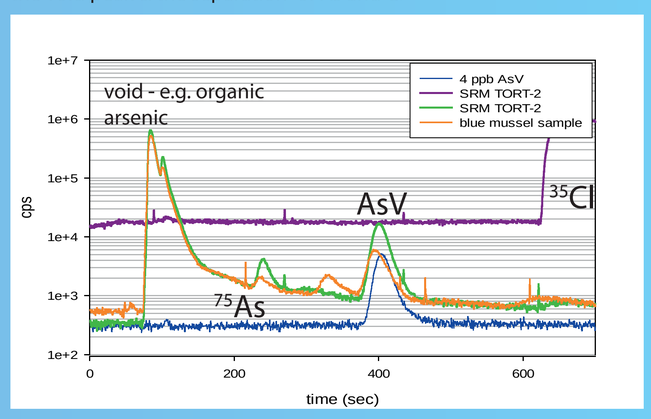
In total 923 individual fish has been analysed for total As. Highest levels were found in a cod sample from the Barents sea (110 mg/kg), a tusk from Skagerrak (89 mg/kg) and a Greenland Halibut (48 mg/kg) from the Norwegian Sea. The largest variation is found in cod from the Barents sea with a concentration range of 0.38-110 mg/kg. In the data no correlation between weight and tAs is observed.
The relatively high concentration found in some samples of tusk may be attributed to the bottom feeding habit while the higher levels in both halibut species and cod may be explained by bioaccumulation.



Inorganic As (iAs)

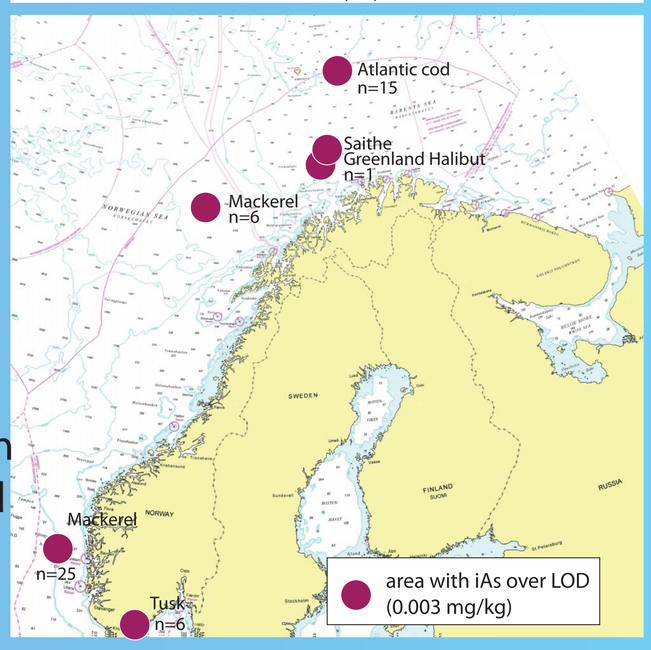
Despite significant levels of tAs, the iAs content of nearly all samples analysed within this study is below the LOD (0.003 mg/kg wet weight). Only a limited amount of samples (n=54) had iAs levels above 0.003 mg/kg wet weight. The highest level are 0. 015 mg/kg wet weight which is still half of the current EFSA opinion.

example of a chromatogramdemostrating the separation of iAs from the void peak & the separation of As and Cl



Geographic variations

No clear statistical indication of regional effects such as pollution or geogenic background on the tAs and iAs levels in seafood is apparent in our datasets yet.



Discussion

iAs levels in seafood from the NOR-economic zone are below the assumed levels in the current EFSA opinion on iAs in food. The data set here shows that iAs levels are generally very low in seafood compared to tAs.

There seems to be some biological factors such as feeding habit and position in the food web effecting the tAs levels in seafood. Bottom feeder and organisms higher in the food web seems to accumulate more tAs compared to lower level pelagic fish species.

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